ELECTROTECHNOLOGY FOR WATER CONDITIONING: A SIMULATION MODEL

V. C. Spinu L. D. Albright Automation in Agriculture, Biological Engineering, Agrarian University of Moldova, Cornell University, 2049 Chisinau, str. Mircesti 44, Riley-Robb Hall, Republic of MOLDOVA Ithaca, NY 14853, U.S.A.

Department of Energy Use and Department of Agricultural and

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Abstract

This paper relates some aspects of an innovative electrotechnological approach focused on improving water quality for horticultural use. Principal processes to condition water for plant growth (related to alkalinity; mineralization; sodium; pH and disinfection) are accomplished in a simple, low-cost, electrolytic unit, which can be affordable for individual growers. Installing such a water conditioning unit directly in a greenhouse achieves additional positive effects. One which makes this technology particularly useful in a greenhouse is the evolution of pure $CO₂$ as a result of bicarbonate ion decomposition.

A simulation model has been developed using EXCEL worksheets to predict the dynamics of all important processes related to water treatment in the electrotechnological unit. This computer model establishes the relationships among (1) design parameters such as the type, number and geometry of electrodes, type of membrane, voltage level applied between electrodes, water flow rate through the treatment chamber; (2) raw water quality parameters such as: total dissolved solids (TDS), concentrations of principal ionic species $(Na^+, Ca^{2+}, Mg^{2+}, HCO_3, SO_4^{2-}, Cl)$, alkalinity, hardness, pH, EC, temperature; (3) the same parameters for water after treatment; (4) regime and efficiency parameters (electrical current applied, electricity and energy consumed per m³ of treated water, current efficiency for TDS removal; and (5) quantities of by-products derived from the processes accompanying operation of an electrolytic water conditioning unit (O_2, CO_2) , base solution).

An analysis of the applicability and efficiency of this electrotechnological approach for improving water quality from the main natural water sources of Moldova was completed using this simulation model. The electrotechnology can contribute efficiently to the successful development of intensive horticulture in Moldova and other regions of the world.

1. Introduction

Water quality is a major concern for greenhouse growers in many regions of the world. Locally available surface water and ground water often can not be exploited for intensive plant growth because of elevated level of mineralization (TDS), alkalinity, sodium, chloride, heavy metals, organic and microbial pollution, etc. When the possibilities of collecting and using rain water are limited, the only alternative for plant growers is to employ an appropriate water treatment technology.

Reverse Osmosis (RO) and Electrodialysis (ED) are the two most popular water purification processes usually recommended to produce high quality irrigation water. ED is considered to be the more economical process for water desalination in the TDS range between 500 ppm and 5000 ppm whereas, in contrast, at concentrations greater than 5000 ppm RO is the less costly process (Strathmann, 1994). In a 2000 hours parallel pilot testing program the Electrodialysis Reversal (EDR) was preferred over RO for desalination of Melvile (Canada) brackish groundwater due to the relative robustness of the EDR system together with its amenability for stop/start operation and insensitivity to lengthy periods without use (Harries, et al., 1991). However, both RO and EDR technologies are relatively expensive in terms of capital, operating, and maintenance costs, making them not affordable for many greenhouse growers.

The term "electrotechnology for water conditioning" stands for all methods that use electricity to improve water quality. In view of this, ED and EDR systems are traditional electrotechnologies for water treatment. This paper relates some aspects of an alternative electrotechnological approach to improve water quality for horticultural use which has been developed at the Agrarian State University of Moldova and at Cornell University. The main objectives of the overall study were: (1) to use electricity to selectively control the levels of the most critical parameters of water for successful plant growth, such as: TDS, alkalinity, pH, sodium, iron, and microbial pollution, and to retain in the treated water the naturally occuring levels of essential nutrients $(Ca^{2+}, Mg^{2+}, SO_4^{2-})$ and micronutrients, (2) to accomplish these processes in a simple, low cost water treatment unit, (3) to develop other specific electrotechnological applications for greenhouse plant growth, especially in hydroponic and closed systems. This report focusses on a simulation model of the processes involved.

Figure 1 illustrates the simplest arrangement and basic operational principles of an electrotechnological unit for water conditioning. The principal elements of such a unit are: the cathode, the anode, the membrane that divides the electrolytic cell into two compartments, and a source of direct current (not shown). Raw natural water to be conditioned is treated with a predetermined specific quantity of electricity in the anode compartment. Electrotechnological water conditioning in this approach is based on several processes and phenomena acting together, the most essential being:

1) electrolysis of water according to the reaction:

$$
2 H_2 O - 4 e^- = O_2 + 4 H^+ \tag{1}
$$

- 2) anodic oxidation of the chloride ions:
- $2 CI 2 e^- = CI_2$ (2)
- 3) electrochemical destruction via anodic oxidation of some inorganic and organic pollutants in water, such as H₂S, CN⁻, and phenol;
- 4) disinfection of water with oxygen, chlorine and other strong oxidant reagents generated in situ in the anode compartment;
- 5) decomposition of the bicarbonate ions in water with the evolution of $CO₂$:

$$
HCO3 + H+ = H2O + CO2
$$
 (3)

which is promoted by the electrolytically produced hydrogen ions.

6) removal of cations $(Ca^{2+}, Mg^{2+}, Na^{+})$ from treated water due to their oriented electrical migration and electrodialysis through a cation exchange membrane. By employing a monovalent cation exchange membrane it is possible to remove sodium selectively from water.

Thus, all the above mentioned processes taking place in the anode compartment contribute to water quality improvement. At the same time a base solution is produced in the cathode compartment as the result of water decomposition on the cathode and the accumulation of the cations transferred from the anode compartment. This base solution can be used for further water and other materials treatment processes.

The performance of an electrotechnological unit for a specific application depends on many factors such as: raw water parameters (TDS, alkalinity, pH, the concentration of Na⁺, Ca²⁺, Mg²⁺, SO_4^2 , CI) and the desired levels of these parameters in the treated water; the unit's design parameters (such as material, number and size of electrodes, arrangement and distance between electrodes, type of membrane employed); the unit's operating parameters (such as voltage applied, intensity of the electrical current, water flow rate or time of treatment, specific quantity of electricity applied); and the quantities of products obtained (O_2, CO_2) , base solution).

The main purpose of this work was to develop a computer model that could establish the relationships among the above enumerated factors and to predict the dynamics of all important processes related to water treatment in an electrotechnological unit. Such a model is needed to fulfill tasks such as estimating the technologies performances in different applications, controlling the process of water conditioning, and designing an appropriate water conditioning system for a specific application.

2. Materials and Methods

Theoretical and experimental investigations focused on developing a simulation model for electrotechnological water conditioning processes in hydroponics were carried out at the Agrarian University of Moldova (Laboratory of Electrotechnology) and at Cornell University (Kenneth Post greenhouses).

Modeling electrotechnology for water conditioning was accomplished using EXCEL worksheets. The algorithmic concept of the model is illustrated in figure 2. Any of the parameters listed in the dashed lined boxes may be input data to the model. Calculated results are listed in the solid line boxes. The central box, outlined with a heavy solid line, signifies unit design parameters that are also inputs to the model and also electrical parameters calculated by the model.

 Formulae used in this model for quantitative calculations were derived by applying the fundamental laws and principles of water chemistry and electrochemistry (the laws of Ohm and Faraday for an electrochimical cell; the Kohlraush's law of independent electrical migration of

ions; the law of electroneutrality and principles of carbonate equilibria in water). In our modeling approach we assumed that:

- 1. Raw natural water to be treated, with TDS in the range of 200-3000 ppm, is a weak electrolyte containing the following 6 essential elements: Ca^{2+} , Mg^{2+} , Na^{+} , SO_4^{2-} , HCO_3^- , and CI. The activity coefficient is equal to unity and remains unchanged during electrolysis.
- 2. Ion concentrations in the water as it is treated are spacially uniform throughout the anode compartment and change in a stepwise, steady-state manner.
- 3. The only anodic reaction during water treatment is the decomposition of water (reaction 1) with concurrent evolution of oxygen and delivery of hydrogen ions into the water.
- 4. Hydrogen ions produced via reaction (1) will be consumed completely for the decarbonation of water via reaction (3) until the residual concentration of bicarbonate ions is 20 ppm (a limit estimated by experiment).
- 5. The quantities of specific cations $(Ca^{2+}, Mg^{2+}, Na^{+}, and H^{+})$ removed from treated water through the membrane is proportional to their partial electrical conductivity, electrochemical equivalent, quantity of electricity applied and permselectivity of the membrane to the specific kind of ions.
- 6. The concentrations of SO_4^2 and CI anions in treated water remain unchanged during the process of electrotechnological water conditioning.

A two-compartment electrolytical unit was fabricated for experimental testing of the mathematical model. A heterogeneous cationic membrane $ULTREX^{TM}$ (Membranes International, Inc.) was used as partition between the anode and the cathode compartments. The cathode was a sheet of stainless steel and the counter electrode was the TIR-2000 DSA oxygen evolving anode a mixed metal oxide catalyst coated on a titanium substrate manufactured by the ELTECH ELECTRODE Corporation. Both electrodes and the membrane were square, having 100 cm^2 of active operating area. The distance between electrodes could be varied from 1 to 10 cm. Depending on the goals of the individual experiments, power supplied to the electrolytical unit was provided in one of two regimes: steady current in the range of 0-3 A or steady voltage in the range of 0-30 V. Water treatment experiments were performed both as batch processes and as flow-through processes with varying water flow rates through the anode and cathode compartments. Adequate laboratory instrumentation and techniques were used to measure the following water treatment parameters: pH, electrical conductivity (EC), alkalinity, hardness, RedOx potential, and the quantities of electrolytically produced gases $(H_2, O_2 \text{ and } CO_2)$.

Modeling the process of electrotechnological water conditioning was performed for the main Moldova natural water sources, using as input the raw water parameters given by Duca et. al.(1995) and Rudic (1993), as well as for municipal water supplied to the Kenneth Post greenhouses.

3.Results and Discussion

Table 1. presents some results derived from modeling the process of electrotechnological treatment of municipal water (Ithaca, NY, U.S.A) which is used as the water source in the Kenneth Post Greenhouses. The validity of these calculations was confirmed by performing relevant measurements in numerous experiments that were conducted with samples of the water.

Water quality undergoes complex and significant changes during the process of anodic electrolytical treatment. From the example shown in table 1 it can be seen that water alkalinity was, in effect, totally removed during the first 18 minutes of treatment using approximately 168 C (Coulomb) of electricity per liter of treated water. Within the same period of treatment the electrical conductivity of water decreased from its initial value of 342 mkS/cm down to 182 mkS/cm but then increased rapidly. The concentrations of Ca^{2+} , Mg^{2+} , Na⁺ ions in the treated water and, correspondingly, the TDS value continuously decreased as more electricity was applied but the efficiency of TDS removal, expressed as grams of removed dissolved salts per kWh of electrical energy consumed, dropped sharply as the process of alkalinity removal ended. Hence, this moment during the treatment, when the point of water neutrality is achieved, is a critical one for the process of electrotechnological water conditioning. In view of this we can define two consecutive stages of electrolytical water treatment: I - bicarbonate zone (water dealkalizing zone) of treatment and II - acidic zone (water acidification zone).

Electrotechnological water treatment within the bicarbonate zone is highly effective in removing alkalinity, TDS, Ca^{2+} , Mg^{2+} and Na⁺ ions, or only Na⁺ ions if a monovalent cation exchange membrane is employed. The highest rates of TDS and specific cations removal in the first period of treatment are assured by the following two factors. First, all H⁺ ions produced via reaction (1) are completely consumed in the process of water dealkalizing according to reaction (3) with the evolution of an equivalent quantity of $CO₂$. Secondly, the concentrations of cations $(Ca^{2+}$, Mg^{2+} and Na^{+}) and, correspondingly, their transference numbers of migration are much higher than those of H^+ ions thus the current passing through the electrolytical unit is used mostly to transfer these cations from treated water through the membrane into the cathode compartment.

Within the second stage of water treatment the acidity of water increases and the rate of salt removal decreases because the concentration and transference number of the hydrogen ions increases continuously relatively to other cations. Electrical conductivity data (table 1) show how greatly the partial electrical conductivity of H ions increases with time and, correspondingly, its role in the electrical migration of cations through the membrane. Electrolytical treatment of water in this zone can be used to produce an excess quantity of acid in water when needed to accomplish the process of water desinfection and for other special purposes such as pH control.

As the case may be, depending on the quality of available supply water and water quality requirements for a certain application, control decisions can be made concerning the duration of water treatment or, in other words, how much electricity to apply to treat a unit volume of raw water. Electrotechnological treatment of water within just the carbonate zone to control alkalinity level, which is accompanied by several additional positive effects such as dissolved salts removal, saturation of water with oxygen, and $CO₂$ evolution, may be of first preference for many horticurtural applications.

The system performances of using electrotechnology just to remove alkalinity from water for some Moldova water sources are presented in table 2. Electrical energy needed for water dealkalizing ranges from approximately 1 kWh/ $m³$ for Nistru water (the principal river of Moldova) to 4.2 kWh/m³ for Leadoveni lake water, which has the highest bicarbonate

concentration. A quantity of 3.2-13 liters of 1 N acid per cubic meter of raw water will be consumed to accomplish the same task using the traditional method of adding acids to remove alkalinity.

During the electrotechnological treatment necessary to remove alkalinity, the concentrations of TDS and particular cations can be reduced by 40-80 % depending on the chemical composition of the raw water. The higher the alkalinity level, the more cations can be removed from treated water.

Rather important are the quantities of by-products obtained while removing water alkalinity using electricity, 126 -565 g of pure $CO₂$ and 24-104 g of pure electrolytical $O₂$ that may saturate water with oxygen. One can benefit from these electrotechnology by-products by installing such a water conditioning unit directly in a greenhouse. Even that part of electrical energy typically considered as lost heat may be considered as a contribution in assisting water temperature control for plant growth. In examples considered in table 2 the temperature of raw water was increased by 0.8-4 $^{\circ}$ C during the electrolytical treatment process. The by-product base solution, which is generally a mix of $Ca(OH)_2$, $Mg(OH)_2$ and NaOH, can be used for water softening, for treating the waste nutrient solution, for plant growth acid substrates, etc.

The same electrolytical unit can be designed to accomplish additionally an accurate pH control of the nutrient solution in a hydroponic system, without chemicals or costly dosage and mixing equipment. Experiments are planned to evaluate the potential of this technology in fighting waterborn disease microorganisms, which can be a major problem in hydroponics, especially in closed systems for greenhouse production.

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Table 1. The dynamics of some essential parameters related to the process of electrotechnological treatment of tap water (Ithaca, NY, U.S.A.).

Natural Water	Concentration of dissolved elements in raw water							Water treatment			Electricity Applied	
Sources from MOLDOVA	(numerator) and treated water (denominator), ppm							by-products, g/m^3			Quantity of	Electrical
	Ca	Mg	Na	HCO ₃	SO ₄	Cl	TDS	CO ₂	O ₂	Base. as $Ca(OH)$	electricity, C/L	Energy, kW*h/m^3
Rivers: 1.Nistru	63 38	18 11	75 49	<u> 195</u> 20	84 84	71 71	<u>506</u> 273	126	24	110	291	0.97
2.Prut	67 36	27 15	83 49	272 20	150 150	$\frac{46}{5}$ 46	645 316	182	33	153	400	1.33
3.Ichel	71 35	70 37	108 60	<u>422</u> 20	221 221	63 63	<u>955</u> 435	290	55	255	665	2.22
Lakes:												
1.Riscani	24 6	<u>49</u> 14	110 32	512 20	$\overline{40}$ 40	<u>14</u> 14	<u>749</u> 127	355	65	302	800	2.62
2.Leadoveni	52 20	78 33	280 125	804 20	293 293	64 64	1571 553	565	104	482	1260	4.20
3.Ialoveni	36 13	51 20	94 39	<u>415</u> 20	92 92	50 50	738 235	271	49	228	595	1.98
Bore-hole Water:												
1.V.Voda	<u>78</u> 36	84 32	124 64	536 20	280 280	53 53	1155 496	372	68	315	821	2.74
2. Telenesti	$\overline{4}$ \mathfrak{D}	33 15	435 211	756 20	429 429	85 85	1742 753	531	99	459	1200	4.00
3.Lunga	88 40	86 43	153 80	598 20	329 329	52 52	1305 564	417	76	354	922	3.07

Table 2. Essential process data of using the Electrotechnology for improving the quality of water from different Moldova water sources.

Figure 1. Schematic diagram illustrating the concept and principles of operation of an electrolytic water conditioning unit.

Fig. 2. The algorithmic concept of the water conditioning electrotechnology model

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